

Sampling and examining deposits from boilers and associated industrial plant —

Part 2: Methods for sampling and examining fire-side deposits

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- Chemical Industries Association
- Department of Industry (Laboratory of the Government Chemist)
- Fabric Care Research Association
- Health and Safety Executive
- Institute of Energy
- Institution of Chemical Engineers
- Institution of Corrosion Science and Technology
- Institution of Gas Engineers
- Ministry of Defence
- National Coal Board
- Royal Society of Chemistry
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Foreword

This Part of BS 2455 was prepared under the direction of the Environment and Pollution Standards Committee.

Revision of BS 2455:1954 "*Sampling and testing of boiler water deposits*" demonstrated a need to add, as a second Part to the revised standard, methods for the sampling and analysis of deposits found on the fire-side of boilers and associated industrial plant. The revised Part 1 "Water-side deposits" was published in 1973, and this Part 2 is complementary to it, containing methods for chromium, nickel and zinc which may be applied to water-side deposits.

Deposits of solid and/or liquid materials (partly-burned fuel or inorganic residues) can be formed on any part of industrial plant through which or over which combustion products pass, for example:

- a) water-tube boilers: burner components, refractories, steam generating tubes, superheater and reheater tubes, baffles, economizer and air heater tubes and plates;
- b) shell type boilers: furnace tubes, burners, smoke tubes, boiler shell, plates and baffles;
- c) ancillary equipment: ash-removal gear, fans, dust-removal plant, hoppers, ducts and chimneys.

Deposits in combustion or flue-gas spaces or in ducting and ancillary plant can interfere with combustion, block gas paths, restrict heat transfer, result in corrosion of the plant or the emission of agglomerated dust as smuts, or disturb normal processes of ash removal. Deposits usually consist of fuel ash and/or corrosion products, but they can also contain residues of deliberate additions to the fuel or combustion air. Their physical form ranges from dense glassy or crystalline slag to fine incohesive dust, often with variations in structure within each specimen according to its location, history or changes in fuel composition or operational practice. Their chemical composition is related to that of the inorganic constituents of the fuel, many of which are volatile and can be considerably enriched by selective condensation, and sometimes to that of the materials of construction of the plant. They may also include organic material from fuel residues.

In this Part of this British Standard, advice is given on procedures for examining and sampling deposits and their substrates in situ, and for subsequent physical examination and chemical analysis of any fractions separated on the basis of evidence so obtained. At every stage, relevant information concerning the fuel composition or operational history should be taken into account when selecting a course of action based on these methods. These methods incorporate the results of many years' experience with a wide variety of plant, and they may be adapted to the examination of related materials, such as boiler clinker or flue dusts.

In any particular investigation the procedures need to be selected as indicated in section 4 to suit the nature of the deposit and the fuel. The amount and location of sampling, together with the extent of photography and laboratory examination, need to be at the discretion of, and by agreement between, the parties concerned.

Deposits that are found during routine examination of the plant need to be assessed with a view to preventing excessive build-up or corrosion of the plant, or excessive emission from the chimney. Deposits also need to be examined in connection with special investigations subsequent to malfunction or plant failure. Material removed during cleaning of the plant is suitable for these purposes, provided that this is sampled with due regard to the purposes of its subsequent examination (see 5.4).

A description of techniques for quantitative sampling of deposits that is relevant to measuring rates of corrosion of plant surfaces has been included.

The scheme for quantitative chemical analysis includes separate determinations, where appropriate, of material insoluble and soluble in very dilute acid: this dilute acid is used to avoid inaccuracies which could result from the hydrolysis of some sulphates if water alone were used. Guidance in the selection of constituents to be determined and evaluation of the results in terms of the causes of their formation or their corrosive potential is included in this standard.

In contrast to Part 1, a scheme of analysis based on the determination of many elements by the atomic absorption technique is provided and this offers considerable advantages in speed and simplicity of manipulation. Alternative methods, mostly colorimetric, are also included (see section 8) for use when atomic absorption is not available; each of these methods is of equivalent performance to the corresponding method in section 7, with the exception of the colorimetric method for zinc, which is less reliable than the atomic absorption procedure.

It is appreciated that the quantity of sample recommended for analysis may not always be available. In such cases, the mass of the test portion will need to be scaled down, which may impose limitations on the scope and precision of the analyses. The report of the results should then include mention of the mass of test portion used.

Attention is drawn to the Health and Safety at Work etc. Act, 1974, and the need for ensuring that the methods specified in this standard are carried out with suitable precautions.

WARNING. The procedures described in the standard methods are intended to be carried out by qualified chemists or other suitably trained and/or supervised personnel.

Normal safety precautions should be observed throughout the use of the methods. Attention is drawn in the text to some specific hazards.

Guidance concerning safety precautions in laboratories can be found in the following publications.

- a) Muir, G.D. (ed.) *Hazards in the Chemical Laboratory*, The Chemical Society, 2nd edition, 1977.
- b) Sax, N.I. *Dangerous properties of industrial materials*, Van Nostrand Reinhold Co., 5th edition, 1979.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 48, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Section 1. General

1 Scope

This Part of BS 2455 describes methods for the sampling and examination of deposits found on surfaces of industrial plant in contact with flue gas.

The methods of sampling and analysis are intended to cover investigation of deposits on superheater and boiler tubes and in combustion chambers, boiler flues, airheaters, economizers and chimneys. In addition, the methods may be applied to deposits in other types of furnaces and in gas turbines. They may be applied also to samples taken from equipment such as probes exposed to the combustion products in order to collect gas-borne material.

NOTE The titles of the publications referred to in this standard are listed on the inside back cover.

2 Definitions

For the purposes of this Part of BS 2455, the following definitions apply.

2.1

deposit

any material that occurs on the surfaces of industrial plant in contact with the flue gas

2.2

dust

non-cohesive solids of particle diameter predominantly less than 1 mm

2.3

soft deposit

a cohesive deposit consisting of loosely adhering particles

2.4

bonded deposit

a cohesive deposit consisting of a solid crystalline matrix containing dust particles

2.5

sintered deposit

a cohesive porous deposit composed of lightly fused particles without an appreciable matrix

2.6

slag

partially or completely fused solid material

2.7

corrosion product

a deposit formed by chemical reaction between gases or deposited material and the constructional material of the plant

2.8

major constituent

a material that constitutes more than 1 % of the test sample

2.9

minor constituent

a material that constitutes 1 % or less of the test sample

3 Reagents, water and apparatus

3.1 Reagents. All reagents shall be of a recognized analytical reagent quality. The reagents referred to in each test method are, as far as possible, those recommended in BS 4245; the preparation of any other reagent mentioned shall be as described in Appendix A.

Industrial methylated spirits is specified in some tests. It should be noted that the use of this material is governed by The Methylated Spirits Regulations, 1983 (SI 1983, No. 252)¹⁾. The methylated spirits shall, when needed, comply with the requirements of BS 3591 and be of a strength of 95 % (V/V) ethanol.

3.2 Water. Subject to the special requirements of certain methods, pure water, having a conductivity of less than 50 $\mu\text{S}/\text{m}$ at 20 °C when freshly prepared and measured out of contact with air, shall be used whenever water is required. This degree of purity can be achieved by distillation or by treating water with the correct grades of ion exchange resins.

3.3 Apparatus. The following British Standards relate to apparatus used for carrying out the tests in this British Standard: BS 410, BS 846, BS 1583, BS 1752, BS 1792, BS 2021, BS 2071, BS 2461, BS 2586, BS 2734, BS 3145, BS 3218, BS 3875, BS 4244 and BS 5922.

¹⁾ Ethanol may be substituted for industrial methylated spirits if desired. However, it is not permissible to use duty-free ethanol, received under the provisions of The Alcoholic Liquors Duties Act 1979, Section 10, for purposes for which industrial methylated spirits is an acceptable alternative to ethanol.

Section 2. Sampling

4 General principles

4.1 Responsibility for sampling. Care in sampling is as necessary as in the subsequent examination, and sampling shall not be delegated to unskilled personnel. The person taking the samples shall have a clear understanding of the purpose for which they are required, and of the appropriate factors involved in operation of the plant.

4.2 Sampling locations. It is not possible to specify sampling locations bearing in mind the wide variety of types of plant covered and their operating conditions. The position from which samples are taken shall be consistent with the aims of the examination and of diagnosing the cause of any malfunction or failure and the subsequent application of corrective measures. If required, photographs should be taken in situ before disturbing the deposits. Sketches of the appearance or to show exact locations of samples are valuable.

Vital information can often be obtained by examining areas of the plant technically related but not necessarily adjacent to a point of failure. If practicable, a portion of the affected part of the plant shall be removed and sent to the laboratory intact.

Information about the development of deposits is often provided by recording their positions relative to the flue gas path. It can also be useful to examine samples of associated fuels, ash or other effluent materials.

4.3 Sample information. The laboratory in which the examination is made shall receive full details of the samples, as described in clause 9.

4.4 Transport of sample. All samples shall be put immediately into chemically inert airtight containers, clearly labelled (see clause 7) and sent to the laboratory as soon as possible.

5 Methods of sampling deposits

5.1 General. It is not possible to put forward any standard procedure that is applicable under the very varied circumstances met with in practice, and no single tool is suitable for removing the variety of deposits which can occur. Sampling, especially from boilers, can be difficult due to inaccessibility and may involve hazards to personnel (see foreword); adequate precautions to conserve the health and safety of those involved shall be taken.

Where a tube has suffered metal failure or serious damage, if practicable it should be removed by cutting at positions about 0.3 m from the damaged area and sent to the laboratory with as much as possible of the associated deposits intact, avoiding contamination during cutting and transport.

In general, inspection, including photography, and sampling of deposits should be carried out as soon as practicable after the plant has ceased operating and before the deposits have been disturbed by any other activity. This is particularly important in at least two circumstances. First, the oxide scale formed on high temperature components of austenitic steels often spalls off during cooling to near ambient temperature, carrying deposits with it. Secondly, some deposits can absorb considerable proportions of water from the atmosphere on cooling, with consequent changes in chemical constitution of the deposit and possible corrosion of the substrate. It can be useful, and may be necessary, to collect certain deposits while the plant is operating. To do this, special probes and tools will be needed.

The composition and structure of deposits vary very much with local conditions within the plant, and every care should be taken during sampling to keep separate the specimens from different positions within a section of the plant, for example from various positions around the circumference of a tube. Occasionally, deposits will be found in positions in which it is apparent that they were not formed: comparison with other parts of the plant may well give a clue as to their origin, but information from “stray” samples should not be relied on without good evidence.

5.2 Adherent deposits and corrosion products. These can vary widely in their hardness, coherence and adherence to the supporting surfaces. Some hard deposits have a loose core or mantle of dust, some dust accumulations are lightly bonded near their surfaces; take separate samples of each fraction. The layers in bonded deposits or corrosion products may be indicative of plant operational history, or result from the gradients of temperature and composition of gas and condensing material through their thickness.

If a deposit separates naturally into fractions during its removal, retain these portions individually; it may be necessary to split coherent samples in the laboratory. In any case, carefully record the physical appearance and behaviour of the deposit during sampling.

Mark off the patch of deposit to be sampled in situ, selected by the responsible person, from the unwanted portion around it. To avoid contamination by the surrounding material clean a band about 25 mm wide and brush away loose material. Remove the sample of deposit down to the bare metal by a suitable tool, in as large pieces as possible and preferably of total thickness.

The removal of adherent deposits is best achieved by using a palette knife or a thin sharp chisel and light-weight hammer; a scoop, shield or bag of plastics film or sheet can often be applied to catch the flying pieces. Close-up photographs may be taken if desired. Should the deposit contain corrosion products, as far as practicable these should be removed and sampled separately. Record the location and nature of corrosion wastage associated with the deposits.

If a boiler is being examined to study the rate of corrosion, remove all of the deposit from a measured area (for example 25 mm × 150 mm) of the surface involved (see clause 6).

5.3 Loose dust and debris. If samples are taken from hoppers, take care to avoid collecting non-representative portions derived from material lodged temporarily on the hopper walls.

In sampling, ensure that representative specimens are taken from any layers or segregations. Large samples of dust may be reduced to a convenient size by quartering. Slag and some bonded deposits are often found as large pieces; it is better to take some of these whole, rather than attempt subdivision in situ.

5.4 Washings and liquid effluents. Where it is necessary to wash sections of the plant for routine or special cleaning, the effluent mixture may be examined. This examination may provide useful information on the fouling or corrosion of the plant, a guide to the disposal of the effluent and the progress of the cleaning. It is not usually practicable to take one sample that would be representative of the whole process. In these circumstances, take a series of samples, each representative of a known volumetric or mass increment of the effluent. A rapid examination of these samples may be made using the methods in BS 1427 and BS 2690, as well as the methods in this document.

6 Quantitative sampling; rate of corrosion

6.1 General. Corrosion of surfaces in contact with flue gases may be detected by physical measurements, e.g. by ultrasonic or calliper measurements, but the rate of corrosion may also be estimated from analyses of deposits collected from the surface. The latter method has the following advantages.

- a) Determinations may be made after a comparatively short period of operation so that operational trials may be carried out quickly.
- b) The rate of wastage may be measured on flat or curved surfaces inside or outside tubes.
- c) The rate of wastage may be determined without cutting a sample from the section under examination.
- d) The technique may be used with coal-, gas-, or oil-firing for low temperature corrosion and with gas- or oil-firing for high temperature corrosion.

6.2 Low temperature corrosion

6.2.1 Preparation for sampling. Low temperature corrosion of airheaters, ducting or other cooled surfaces in contact with flue gas normally occurs in localized zones where the temperature is below the acid dew-point. To measure the rate of wastage, first clean the selected zones down to metal (washing with water is generally adequate). Then operate the plant for a period that allows sufficient deposit to form to enable a representative sample to be collected but not so long that deposits flake off the surface. A period of 200 h to 2 000 h is generally suitable.

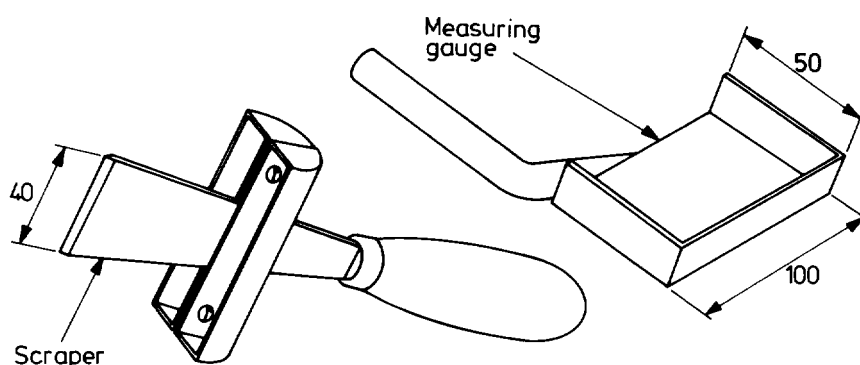
6.2.2 Apparatus. Suitable forms of scraper for the collection of samples are shown in Figure 1 and Figure 2.

6.2.3 Sampling of deposits from plate-type airheaters and ducting. The coldest zone, where corrosion is likely to be most severe, is where the air enters and the flue gas leaves.

A cold zone subject to corrosion may be caused by inadequate insulation, local cooling at flanges or ingress of air.

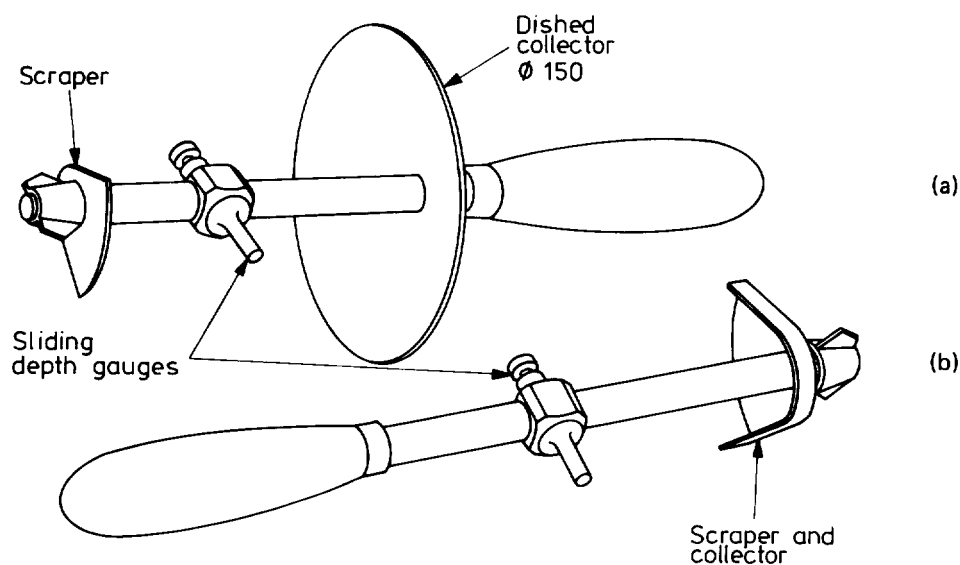
Take samples from a measured area with a scraper and measuring gauge similar to that shown in Figure 1. When collecting deposit from the lower section of an airheater, place the measuring gauge against the flat surface without disturbing the deposit. Using the scraper, scrape off the plate all the deposit enclosed by the gauge and collect it in the hopper as it falls from the plate. Thus, the deposit will have been removed from an area of 5 000 mm². Use the same technique for sampling from the ducting.

Collect deposit from the upper section of an airheater by placing the gauge against the flat surface of the plate without disturbing the deposit. Then scrape off the deposit and collect it in the base of the gauge. Carefully draw the gauge upwards until the lower edge is almost up to the top of the plate, tilting it away from the plate so that all of the deposit is retained by the gauge, lift it out and transfer the deposit to a suitable container.



All dimensions are in millimetres.

Figure 1 — Scraper and measuring gauge for use with plate-type airheaters and ducting



Dimension is in millimetres.

Figure 2 — Scrapers for use with vertical tube airheaters

6.2.4 Sampling of deposits from vertical tubular airheaters. Use the scraper and depth gauge shown in Figure 2(a) or Figure 2(b) for obtaining deposit from a known area of a tubular type airheater, that is with flue gas passing through the tubes.

Collect deposits from the surfaces of tubes at the bottom of an airheater bank with instrument (a).

If the deposit is more than 1 mm thick, fix the sliding depth gauge 50 mm from the scraper. Insert the scraper upwards into the tube without disturbing the deposit until the depth gauge contacts the bottom of the tube. Scrape off all the deposit from the bottom 50 mm of the tube and collect it in the dished collector as it falls from the tube. Knowing the internal circumference of the tube, the area from which the sample has been collected can be calculated.

If there is only a thin layer of deposit, up to 1 mm thick, fix the depth gauge 150 mm from the scraper to enable a sample to be obtained from a larger area.

If the deposit is very thick so that it is not possible to insert the scraper without disturbing some of it, scrape the deposit from half the circumference of the tube, without disturbing the other half and discard it. Then slide the scraper up the cleaned surface without disturbing the remaining deposit, turn it through 180° and scrape the deposit off into the dished collector and transfer it to a suitable container.

Collect deposit from the surface of tubes at the top section of an airheater with instrument (b).

Use the adjustable depth gauge in a manner similar to that described for instrument (a). Insert the scraper downwards into the tube until the gauge contacts the top of the tube. Scrape the deposit from the tube by drawing the scraper upwards a number of times until the deposit has been completely scraped off the area under investigation. The deposit falls into the scraper, which shall be slightly dished to ensure that all is collected. Then withdraw the scraper from the tube and transfer the deposit to a container.

If the deposit is very thick, half the circumference of the tube may be cleaned, as described previously, before inserting the scraper and turning it through 180°.

In some tubular airheaters, the air flows through horizontal tubes and gases flow across the tubes. Scrape samples from a measured area of the tube and collect them in a suitable tray.

6.2.5 Calculation of the rate of wastage of an airheater or ducting. At least duplicate samples shall be scraped off the surface in the selected zones. The deposit collected from each zone shall be weighed and the soluble iron content determined (use solution K; see 23.5). Knowing the period of operation since the surface was previously cleaned and the area from which the sample was collected, the rate of wastage, in millimetres per 1 000 hours, is given by

$$\frac{0.09X}{q}$$

where:

X is the concentration, in milligrams of Fe_2O_3 per square centimetre per 1 000 hours;

q is the percentage by mass of Fe in the tube metal.

6.3 High temperature corrosion. Superheaters and tube supports may be subjected to corrosion due to attack by constituents of the flue gases from gas-, oil- or coal-fired boilers. It is possible to measure the rate of wastage of superheaters by the iron content of the deposits. These deposits are frequently not water-soluble, however, and therefore it is not possible to use the same technique as with the products of low temperature corrosion.

When oil- or gas-firing is used, it can be assumed that the total iron content of the deposit is almost entirely the product of attack on the tubes, but with coal-firing a considerable portion of the total iron content usually is from the fly ash. Measurement of the rate of wastage of superheaters and tube supports by analysis of deposits is, therefore, usually only applicable to oil- and gas-fired plant.

The zones from which samples are to be taken shall generally be those where the highest metal temperature is known or anticipated to occur. First clean these zones down to the metal by scraping with a suitable steel blade or abrasive material. Then operate the boiler for a suitable period; 1 000 h to 4 000 h is generally adequate. When the boiler is withdrawn from service scrape duplicate samples off the surface in selected zones and measure the area from which the deposit has been removed.

The soluble and insoluble iron contents shall be determined in the deposit (use solutions K and M, see 23.5 and 25.1.3). The rate of wastage shall be calculated as for low temperature corrosion, except that it shall be based on the total iron content instead of the soluble iron content.

7 Labelling of samples after collection

The following information shall be written on the label accompanying the sample:

- a) identification of plant from which the sample was taken;
- b) exact position from which the sample was taken;
- c) identification code of sample;
- d) date and time of sampling.

8 Detailed information about sample

The following detailed information about the sample shall be recorded:

- a) identification of plant and name and address of owner;
- b) exact position from which the sample was taken, giving details of section or sub-section of plant;
- c) identification code of sample;
- d) date and time of sampling;
- e) purpose of investigation;
- f) detailed method of sampling;
- g) date of previous inspection of plant, and subsequent operational history, if known;
- h) description of deposit;
- j) identity of responsible sampler.

Section 3. Physical examination

9 Visual examination

Deposits from the fire- or gas-side of industrial plant may reach the laboratory in a variety of forms and conditions. Almost certainly, they will be heterogeneous and may show laminations built up at different times in the history of the plant.

Make a thorough visual examination of the sample using a hand lens and record the observations. The deposit may be photographed and a piece of the sample retained in its original form for further microscopic examination and future reference.

The preparation of each test sample shall be regarded as a separate problem depending on its nature, and the method adopted shall be recorded.

Deposits may be received either still attached to, or detached from, a supporting plant surface. In either case, use appropriate tools to separate and break the deposit so as to minimize contamination by extraneous material. When removing the sample from a support surface take special care to avoid metallic contamination. If samples are laminated and it is desired to examine each part individually, the component fractions should be separated as a first step in the preparation. Differences between the magnetic susceptibilities of fractions may be used to separate them.

NOTE A deposit may consist of crystals of different composition and a knowledge of the nature and form of the various constituents present can frequently be of considerable value in diagnosing the conditions that have existed in the section of plant from which the sample was taken. The compounds present in a deposit usually cannot be identified by chemical analysis alone.

10 Microscopic examination

Microscopic examination of boiler deposits may indicate the mode of formation of the deposits, particularly when supplemented by chemical analysis of the deposits. Separate any distinct layers by using a knife to break off a small portion of each of the layers and examine them separately.

For some deposits additional information may be obtained by extracting them with water and examining the insoluble residue. Prepare the insoluble residue by placing a small, lightly crushed, portion (e.g. 1 mg to 10 mg) of the test sample or separated layer in a test tube with a few millimetres of 0.04N perchloric acid solution (see A.22) and boil until it is observed that no more sample will go into solution. Decant and discard the solution and wash the residue with water; dry it and prepare it for examination under the microscope.

Mount the test samples or separated layers and/or insoluble residues on slides and examine them with a microscope at a magnification of $\times 10$ to $\times 100$, using primarily oblique top lighting. Typical observations and the inferences that may be drawn are given in Table 1.

11 Other instrumental methods

Microscopic examination may help to identify the substances present in the deposit but a more generally useful technique is X-ray powder diffraction analysis. In this, a diffraction pattern is obtained, which is made up of the patterns characteristic of the crystalline constituents present. Identification can be made by comparison with reference patterns of pure substances or known mixtures. Both techniques have their limitations as only the major crystalline constituents can be identified, not minor constituents or amorphous materials, although the presence of major proportions of glass can be discerned.

X-ray fluorescence spectroscopy is sometimes applied with advantage to the examination of deposits and, where applicable, will conveniently be substituted for the methods for qualitative examination (see clause 15).

Other physical methods for determining the structure present, such as infra-red spectroscopy or Raman spectroscopy, can provide useful information.

Table 1 — Microscopic examination of deposits

Source of sample and fuel	Test sample or separated layer	Insoluble residue	Inference
Combustion chamber Coal or oil	Dark fused deposits with few spherical or coke-like particles present. Gas holes.	Similar to test sample	Very high temperature deposits in which the fly ash has re-fused. If tube wasting has occurred it may be associated with flame impingement. Analysis expected to show low alkali metals and sulphate contents, each below 5 % (<i>m/m</i>).
Combustion chamber; radiant surfaces Coal	Sintered deposit with spherical particles or other fly ash: spherical particles, frequently coloured, may be observed fused together.	Similar to test sample	High temperature deposit, possibly from a coal with a low ash-fusion point. Analysis expected to show low alkali metals and sulphate contents.
Combustion chamber; high temperature convective surfaces Coal or oil	Whitish crystalline mass with embedded spherical particles.	Spherical particles frequently light red or clear. Coke-like particles and very little crystalline material.	Typical of deposits found in the superheater and reheater zone. Alkali metal-matrix type deposits associated with fuel with a high inorganic salt content. Analysis expected to show high alkali metals [10 % (<i>m/m</i>) to 20 % (<i>m/m</i>)] and sulphate [20 % (<i>m/m</i>) to 40 % (<i>m/m</i>)] contents.
High temperature convective surfaces Coal	Clear crystalline deposits of ice-like appearance and with very few spherical particles.	Similar to test sample	Phosphatic deposits, usually found only in stoker fired plant, due to a high percentage of phosphates in coal. Forms a hard water-insoluble shell on superheaters.

Table 1 — Microscopic examination of deposits

Source of sample and fuel	Test sample or separated layer	Insoluble residue	Inference
High temperature convective surfaces Oil	Dark acicular crystals with a few coke-like spheres.	Similar to test sample	Typical of superheater deposits in oil-fired boilers. Analysis expected to show high sodium [10 % (m/m) to 20 % (m/m)], vanadium [20 % (m/m) to 50 % (m/m)] and sulphate [10 % (m/m) to 30 % (m/m)] contents.
Moderate temperature convective surfaces Coal	Mainly spherical and coke-like particles A little crystalline material.	Spherical and coke-like particles. Spheres generally colourless, white or black. In higher-temperature zones some of the spheres may be red.	Fly ash predominates. Crystalline material is water-soluble alkali sulphates. Bonding is usually slight. Corrosion is unlikely. Some deposits are hard and bonded. Analysis of these expected to show high calcium and sulphate contents.
Moderate temperature convective surfaces Oil	Coloured crystalline deposits with a few embedded spherical and coke-like particles.	Spherical and coke-like particles.	Typical or primary superheater, low temperature reheater and economizer deposits. Analysis expected to show high sodium, vanadium and sulphate contents.
Low temperature surfaces Coal or oil	Crystalline with a few embedded spherical and coke-like particles. Frequently deliquescent.	Mainly coke-like particles. Some black or white spherical particles from coal-firing.	Typical of deposits from an airheater, economizer or ducting where low temperature corrosion can occur. Analysis expected to show high soluble iron [10 % (m/m) to 30 % (m/m)] and sulphate [> 20 % (m/m)] contents, and high acidity.
Low temperature surfaces Coal or oil	Mainly spherical and coke-like particles with little crystalline material.	Spherical and coke-like particles.	Typical of deposits from airheater, economizer or ducting without significant low temperature corrosion. Analysis expected to show low soluble iron and sulphate content.

Section 4. Scheme for examination

12 General

The Chemical characteristics of deposits that form on the fire-side of the plant depend on the local temperature and on the composition of the inorganic constituents of the fuel. Variations in the scheme of analysis are necessary to obtain useful information about the characteristics of deposits collected from different sections of the plant and according to the fuel used, coal, oil or gas (see note). If both coal- and oil-firing are used, either together or alternately, deposits should be analysed for both types of constituents. Inorganic constituents introduced during the use of additives and by known or suspected contamination should be included in the analysis.

Methods for determining the solubility in 0.02N perchloric acid and the soluble constituents are included. It may be useful to determine some of the minor constituents listed in clause 13 as additional soluble constituents.

The solubility of deposits from high temperature surfaces indicates the type of bonding that is causing the deposit to adhere to the surfaces and also acts as a guide to the most suitable method for removing the deposits.

Analysis of the soluble fraction from low temperature surfaces, below 200 °C, provides information on the amount of iron that has been removed from the surfaces due to acidic corrosion. Based on the concentration of soluble iron and using the technique for collecting the deposits on a quantitative basis, it is possible to assess the rate of wastage of the heat exchange surfaces (see 6.2.5). In addition, the acidity of the soluble fraction indicates the corrosive characteristics of the deposit.

Fire-side deposits may contain the residue of incompletely-burned fuel, mostly carbon. This is best determined directly as carbon (see clause 17) but an estimate may be made by determining the loss on heating between 380 °C and 815 °C (see clause 20). This loss on heating is usually higher than the carbon content (details of other contributory constituents are described in the note to 20.2) and the measurement should be used as a reasonably accurate guide to the carbon content only when it exceeds 5 % (m/m) of the dry sample.

The major constituents should normally be determined, but the minor constituents should also be determined in special circumstances, dependent on the purposes of the examination. Although nearly all naturally-occurring elements may be present in these deposits in at least trace quantities, occasionally some constituents, other than those listed in clause 13, are present in significant proportions, possibly due to extreme variations in fuel composition or unusual operational circumstances leading to enrichment in particular localities in the plant. Those listed in clause 13 as “minor” can also sometimes occur as “major” constituents. In addition, other elements may occur as minor constituents but, because justification for their inclusion in a scheme of analysis is rare, methods for their determination are not quoted in this standard; examples are copper, germanium, lithium, manganese, molybdenum, tin, titanium.

If soluble material amounts to less than 10 % (m/m) of the test sample then the constituents of the water soluble fraction should be regarded as minor constituents.

NOTE Where gas-firing is used, the concentrations of deposit-forming constituents in the fuel are generally so low that they cause no problem. The schemes described are primarily for deposits collected from coal- or oil-fired boilers but they will be useful for deposits formed from other fuels.

13 Constituents for determination

13.1 Deposits from the combustion chamber, superheater, reheater, convection surfaces above 200 °C in boilers

13.1.1 *Coal-firing.* The following constituents should be considered:

Major constituents	Minor constituents
Aluminium	Arsenic
Calcium	Barium
Iron, ferrous	Boron
Iron, total	Chloride
Magnesium	Chromium
Potassium	Lead
Silicon	Nickel
Sodium	Phosphate
Sulphate	Sulphide
Soluble material	Zinc
Soluble portion	
Acidity	
Aluminium	
Calcium	
Chloride	
Iron, total: ferrous; ferric	
Magnesium	
Potassium	
Sodium	
Sulphate	

13.1.2 Oil-firing. The following constituents should be considered:

Major constituents	Minor constituents
Iron, ferrous	Lead
Iron, total	Magnesium
Nickel	Potassium
Sodium	Sulphide
Sulphate	Chromium
Vanadium	
Soluble material	
Soluble portion	
Acidity	
Iron, total: ferrous; ferric	
Sodium	
Sulphate	
Vanadium	

13.2 Deposits from the low temperature zone, below 200 °C surface temperature. With coal- and oil-firing these deposits are normally examined to assess corrosion and blockage due to the deposition of acid. In this context it is usually necessary to consider only the following:

Major constituents and properties	Minor constituent
Carbon	Chloride
Free acidity and pH of aqueous extract	
Iron, total	
Potassium (coal only)	
Sodium	
Sulphate	
Vanadium (oil only)	
Soluble material	
Soluble portion	
Acidity	
Chloride	
Iron, total: ferrous; ferric	
Potassium (coal only)	
Sodium	
Sulphate	

For a fuller examination of these deposits the other constituents in **13.1** should be considered.

14 Preparation of test sample

14.1 The analytical investigation is best carried out on a dry test sample. An outline of the method for preparing test samples from most types of deposit is given in Figure 3. Some deposits require variations on this procedure; these are described in **14.2**.

Heat all laboratory samples in an oven at 105 °C to 110 °C for a period of 2 h; record the resultant percentage loss in mass of the sample.

14.2 Break or crush the dry solids into pieces of a size (not larger than 5 mm) suitable for grinding in a mortar and then, if necessary, reduce in mass by quartering to a total mass of sample not exceeding 20 g. Grind this material to pass entirely through a test sieve of 250 µm nominal aperture (see BS 410). Use this sample in all determinations where more than 0.1 g of the test sample is taken. Take at least 0.5 g of this ground sample and grind it further to pass entirely through a test sieve of 63 µm nominal aperture (see BS 410); use this finely ground sample in all determinations where 0.1 g or less of the test sample is taken (see clauses **18** and **22**). If on inspection the 250 µm sample is observed to consist of widely different sized particles the sample should be further ground to pass entirely through a test sieve of 63 µm nominal aperture.

The presence of oil or free sulphuric acid may cause difficulty in crushing or grinding the samples to the requisite particle size. Such samples should be crushed as fine as is practicable and a portion of the well-mixed product used for qualitative analysis (see clause **15** and the final paragraph of this clause) and for determining oil (see clause **21**), free acidity (see clause **19**) and soluble material (see clause **23**). A sufficient quantity of the dried insoluble residue (see clause **19** or clause **23**) should then be ground to pass entirely through a test sieve of 250 µm or 63 µm aperture (see BS 410) to provide the dried test sample for other determinations.

If it is necessary to examine washings from the surfaces of the plant, filter these and analyse the filtrate and solids separately.

Bottle each test sample and label the container with a description of the contents.

If it is not apparent whether the sample contains oil or sulphuric acid, test it as follows. Heat to red heat a piece of clean platinum foil, nickel foil or porcelain, between 1 cm² and 5 cm² in area, and allow it to cool out of contact with any organic material or acid. Place a few milligrams of the laboratory sample on this support and heat it gently at first, then to red heat. The evolution of oily and acidic vapours may be distinguished respectively by their odour, and by exposing them to a moistened pH indicator test paper. The presence of free acid may be confirmed by testing an extract of a few milligrams of the sample in 1 ml of water with a pH indicator test paper: a pH value of less than 3 indicates the presence of free acid.

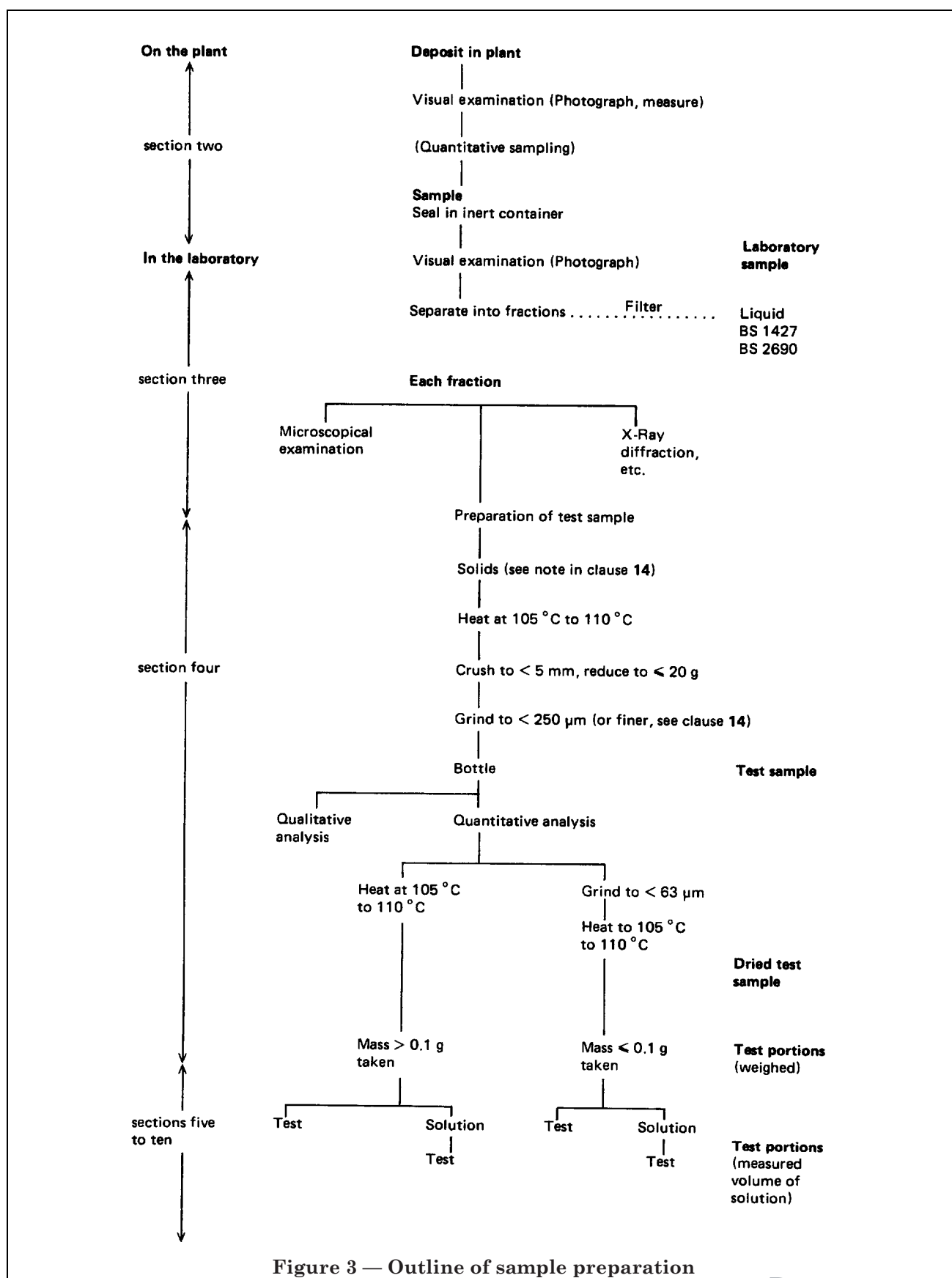


Figure 3 — Outline of sample preparation